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[Re₂(CO)₉]²⁻ on Hydroxylated MgO: Formation from [Re₂(CO)₁₀] and Evidence of Ion Pairing at the Surface

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Beamline: X11A

[Re₂(CO)₁₀] is physically adsorbed on almost fully dehydroxylated MgO powder, but it is chemisorbed on hydroxylated MgO, forming [Re₂(CO)₉]²⁻, as demonstrated by the infrared spectra of the surface species and by extraction of the adsorbed anion into solution by cation metathesis. By comparison with the analogous solution chemistry, the chemisorption on MgO is inferred to involve nucleophilic attack of surface OH groups on CO ligands of [Re₂(CO)₁₀] to give [HRe₂(CO)₉]⁻, which is deprotonated on the basic surface to give [Re₂(CO)₉]²⁻. Comparison of the infrared spectra of the surface species with those of salts of [Re₂(CO)₉]²⁻ in various solvents, combined with ultraviolet-visible spectra of salts of [Re₂(CO)₉]²⁻ in various solvents, demonstrates that [Re₂(CO)₉]²⁻ is strongly ion paired with the MgO surface.